

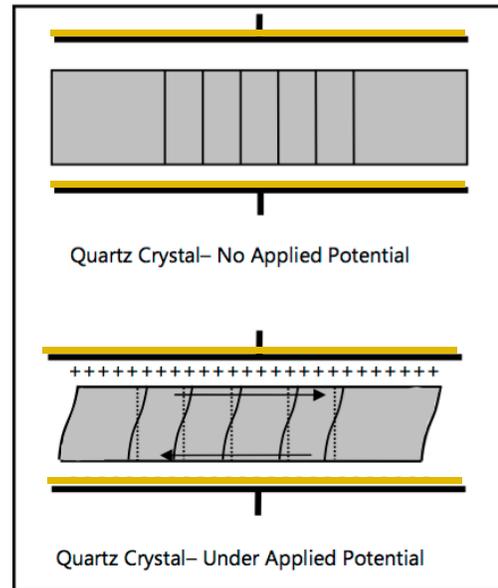
# Electrochemical Quartz Crystal Microbalance (eQCM)

## 1. Fundamentals

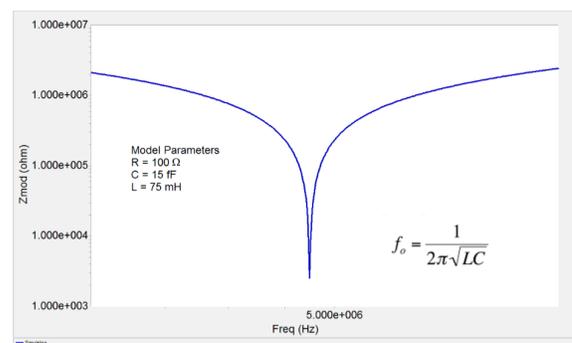
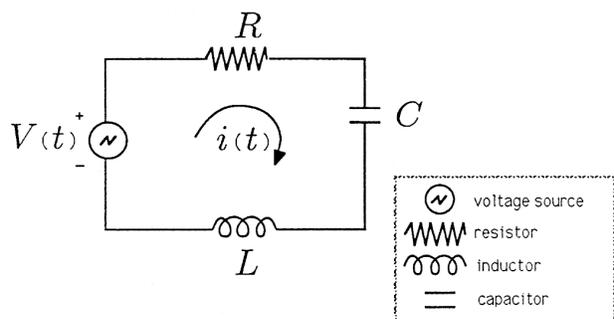
The quartz crystal microbalance (QCM) is based on the piezoelectric effect. This is where a crystal produces a potential across a material in response to a mechanical strain. The converse is also true, a mechanical strain can be produced by application of a potential across a material. Quartz is by far the most commonly used due to its availability and many different ways to cut the crystal.

Application of an alternating potential (sine wave) to the crystal faces causes the crystal to oscillate. A standing wave within the crystal can be established and (**Figure 1**) the frequency of this oscillation is called the resonate frequency. This fundamental frequency can be calculated based on the properties of the crystal.

The quartz crystal oscillations can be modeled in a similar fashion to a mechanical spring-mass-damper simple harmonic oscillator or an electrical RLC circuit. In the case of an RLC circuit (**Figure 2a**), R represents the energy dissipated during the oscillation, C represents the energy stored and L represents the inertial component related to the displaced mass. Therefore, the impedance spectrum of the quartz crystal can be used to extract the values of R, L and C. An example Impedance spectrum for a RLC circuit is shown in **Figure 2b**. Here, a sharp spike is observed at the resonate frequency ( $f_0$ ) and therefore a change in mass results in a change in frequency .

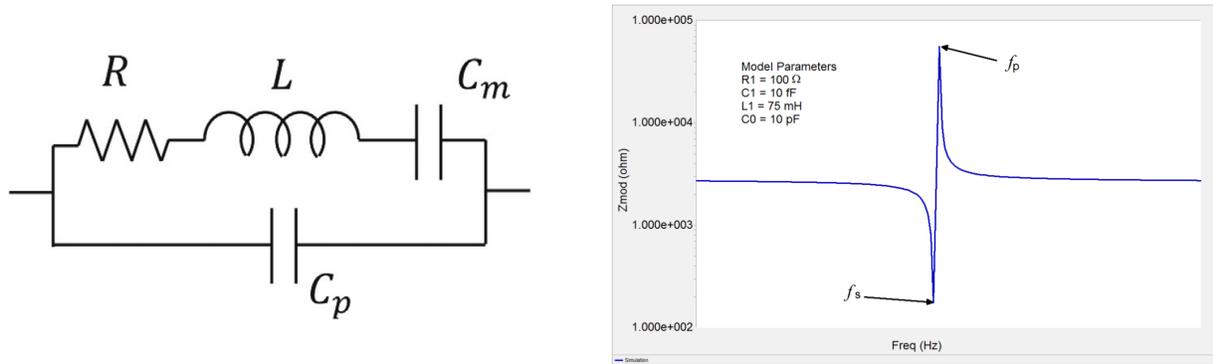


**Figure 1.** Scheme of QCM Shear deformation



**Figure 2. (a)** Scheme of an RLC Circuit for modeling the Impedance response of a quartz crystal **(b)** Impedance spectrum for a series RCL circuit

In practice, the act of adding electrical contacts to the crystal (represented as gold contacts in **Figure 1**) adds an additional capacitance. This capacitance is added into the RCL model and is denoted the Butterworth-Van Dyke (BVD) Model (**Figure 3a**). This circuit model results in two resonant frequencies  $f_s$  and  $f_p$ , (**Figure 3b**) which represent the series resonant frequency (same as the original RLC circuit in **Figure 2a**) and parallel resonant frequency. In the example of the Stanford Research Systems (SRS) QCM, the parallel capacitance is manually canceled out on the front of the instrument and the series resonant frequency is measured.



**Figure 3.** (a) Equivalent circuit for the Butterworth-Van Dyke Model (b) Impedance spectrum for the BVD model

As previously mentioned, the resonant frequency is dependent on the inductor element, which itself is a function of the mass displacement, therefore, the mass change of the quartz crystal can be correlated with a change in the resonant frequency. This dependence is represented as the Sauerbry equation (**Equation 1**) and can be further simplified to **Equation 2** where  $C_f$  is the calibration constant. This constant is usually  $56.6 \text{ Hz cm}^2 \mu\text{g}^{-1}$  for a 5 MHz At-cut quartz crystal in air, however it is recommended to calibrate each crystal individually. Additionally this analysis assumes a thin rigid film and the decrease in frequency is small in comparison to the resonance frequency (5 MHz).

$f_0$  - Fundamental frequency of crystal (5 MHz);

$\mu_q$  - Shear modulus of crystal

$\rho_q$  - Density of the crystal

$m$  - Mass added

$n$  - Harmonic number ( $n=1$ , 5 MHz driven at 5 MHz)

$$\Delta f_s = -\frac{2f_0^2 mn}{(\mu_q \rho_q)^{1/2}} \quad (1)$$

$$\Delta f = -C_f m \quad (2)$$

## 2. Setting up the Experiment

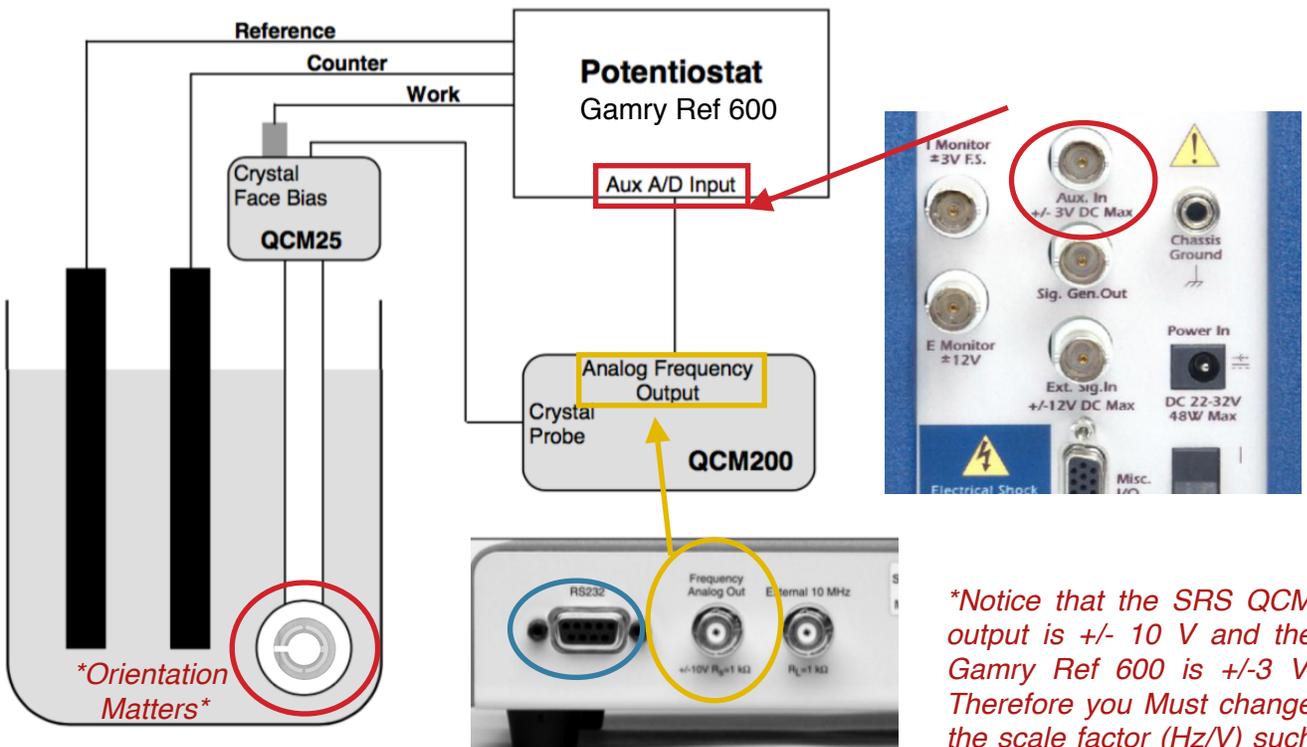
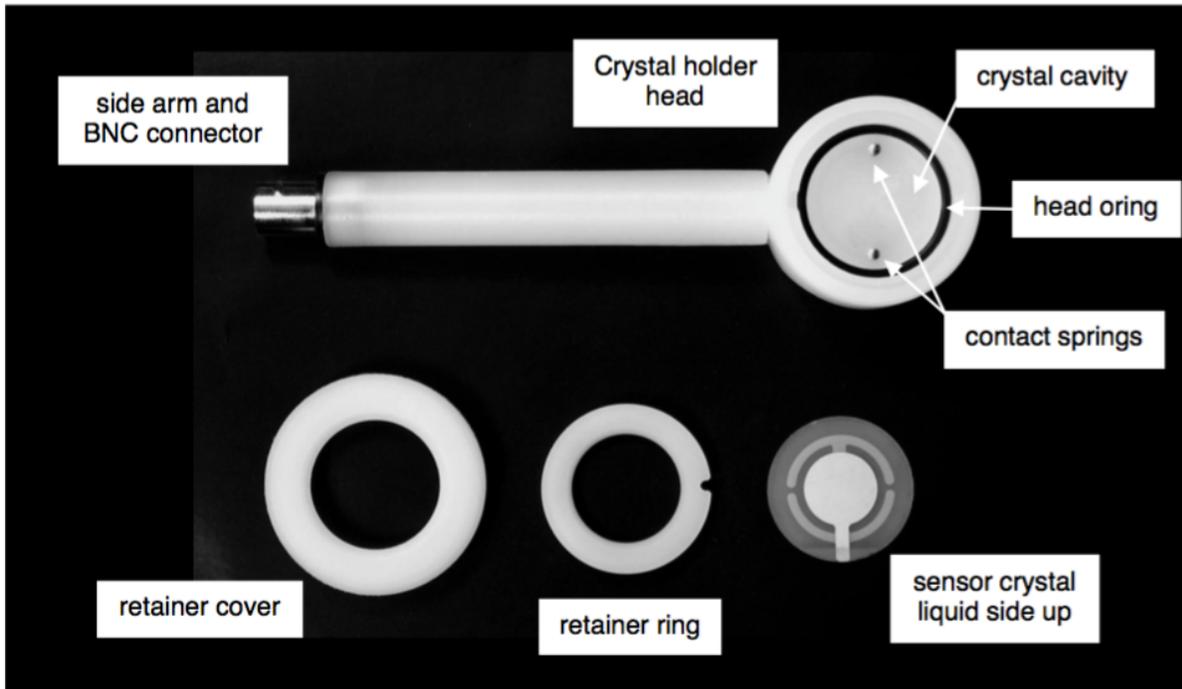


Figure 4. Instrument setup for eQCM To PC

*\*Notice that the SRS QCM output is +/- 10 V and the Gamry Ref 600 is +/- 3 V. Therefore you Must change the scale factor (Hz/V) such that the output is between +/- 3V\**

The above setup is for eQCM and the SRS QCM doesn't need to be connected to the potentiostat if the mass change is not an electrochemical process. In addition to setup, the glass cell containing the solution must be sealed to the face of the eQCM. It is recommended that the cell have a water jacket in order to stabilize the temperature of the crystal environment. Additional details on how to assemble the electrode and electrode connections is provided in the SRS QCM manual and a video is available online at <http://www.thinksrs.com/products/QCM200.htm>

### 3. Experiment : Calibrating the Quartz crystal microbalance by $\text{Cu}^{2+}$ electrodeposition

1. Prepare an aqueous electroplating solution consisting of 10-100 mM  $\text{CuSO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$ . In this example the copper sulfate is 50 mM
2. Estimate the change frequency ( $\Delta f$ )
  - In this experiment, a constant current plating and stripping process will be used to calibrate the sensitivity factor ( $C_f$ ). The first step will be Cu plating for 50 seconds at a rate of -1.0 mA. This results in 0.05 C of charge being passed. The next step will be Cu stripping for 50 seconds at a rate of + 1.0 mA. The expected frequency change can be calculated from the area (A, 1.38  $\text{cm}^2$ ), molecular weight (Mw. Cu = 63.54 g/mol), Faradays constant (F), number of electrons transferred (n, for  $\text{Cu}^{2+}$  n = 2) and the estimated sensitivity factor (Cf, 56.6  $\text{Hz cm}^2 \mu\text{g}^{-1}$  for a 5 MHz At-cut quartz crystal) using the following equation. In this example the expected frequency change is ~ **675 Hz**.

$$\Delta f = \frac{10^6 \cdot M_w \cdot C_f \cdot Q}{n \cdot F \cdot A} \quad (3)$$

- **IMPORTANT:** The analogue frequency output of the SRS QCM will output a voltage proportional to  $\Delta f$ , the proportionally factor can be set on the instrument display. The scale factors can be set to the following (200 Hz/V, 500 Hz/V, 1 kHz/V, 2 kHz/V, 5 kHz/V, 10 kHz/V, 20 kHz/V.) Remember the output could be +/- 10 V, However the voltage **MUST be between +/- 3V for the Gamry Ref. 600 to read.**
- Therefore, in this example the scale factor will be set to **500 Hz/V** in order to ensure that the frequency change ( $\Delta f$ ) is within +/- 3 V.

3. Fill Electrochemical cell and immerse the reference electrode (Ag/AgCl Sat. KCl ), counter electrode (graphite rod or platinum mesh) and working QCM electrode as shown in **Figure 4**.
4. Once immersed in the solution, flip the  $C_o$  compensation switch to [ADJUST], the lights will turn on, then adjust the dial up/down until only the illuminated lights are reading [NULL]. This is the manual capacitance compensation as previously mentioned. After this process, flip the  $C_o$  compensation switch back to [HOLD]. This compensation process should be repeated every time the environment of the crystal/electrode changes.
5. The [PARAMETER] button on the front of the display is used to cycle through all the available options (Gate interval (0.1 s), Scale Factor, Frequency, Resistance). The [VALUE] button is used to cycle through the frequency and resistance display modes which include the following (F: Absolute Frequency, f: Relative Frequency, m: mass displacement [ng] = relative frequency/ 0.0566, R: Absolute Resistance , r: Relative Resistance).
6. Set the display to relative frequency (f), then hold down the [VALUE] button in order to zero the relative frequency. This is the value that will be output to the Gamry REF 600 using the following equation. Analogue Frequency out [V] = Relative Frequency/-Scale Factor. The Scale factor is set using [PARAMETER] and [VALUE] buttons to find and change the current scale factor (set **500 Hz/V**). \*The positive voltage direction indicates an increase in mass and the more negative, a mass decrease, Hence the negative sign in the equation\*
7. Open SRSQCM on the Desktop or by going to the folder C:/srsqcm200/ srsqcm200.exe. Also open up Gamry Framework.
8. Allow the QCM to stabilize after coming into contact with the liquid. Purge the solution with argon. Turn off Ar purge while experiment is running in order to minimize interference with any changes in pressure. Also eliminate any external vibrations.
9. Start collecting data by clicking the red [(click to run)] and [LOG DATA] button, then select where to save the data. **zero the relative frequency** by holding the [VALUE] key on the front of the SRSQCM200.

10. Configure the Gamry chronopotentiometry experiment in the following way

**Pre Step Current:** 0 A  
**Pre Step Delay:** 10 s  
**Step 1 Current:** - 0.001 A  
**Step 1 Time :** 50 s  
**Step 1 Current:** + 0.001 A  
**Step 1 Time :** 50 s  
**Sample Period:** 0.1 s  
**Upper Voltage:** 1.0 V  
**Lower Voltage :** - 1.0 V  
**Advanced Pstat Setup :**

Another window will open, select the following options

CA Speed : Norm

Ich: 5Hz

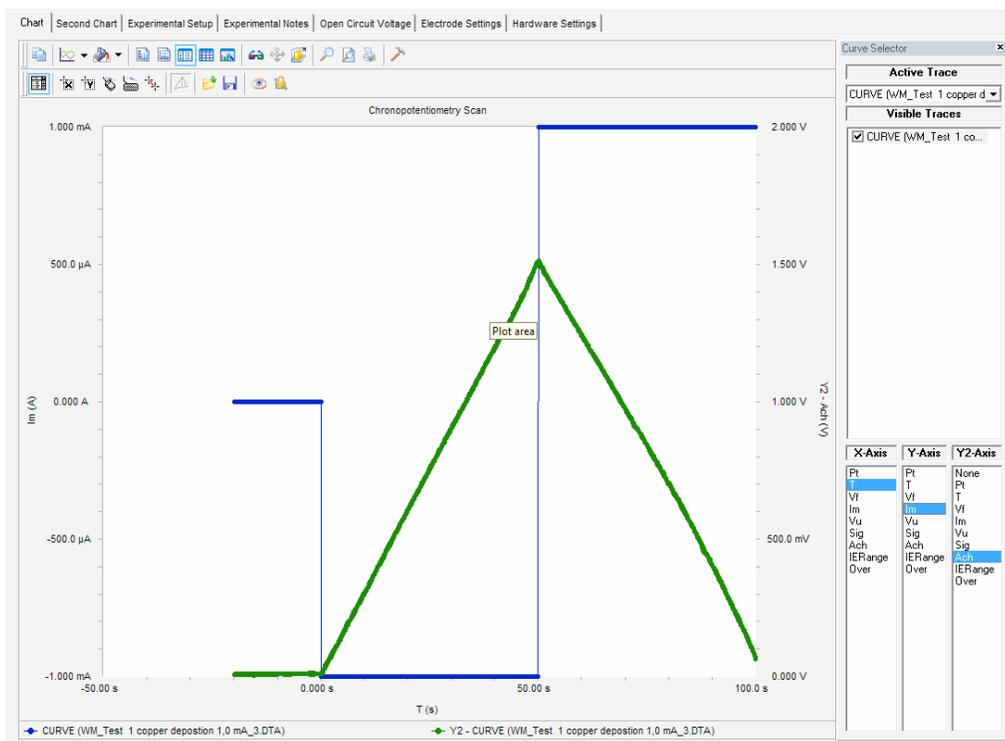
Vch: 5Hz

Ach : BNC

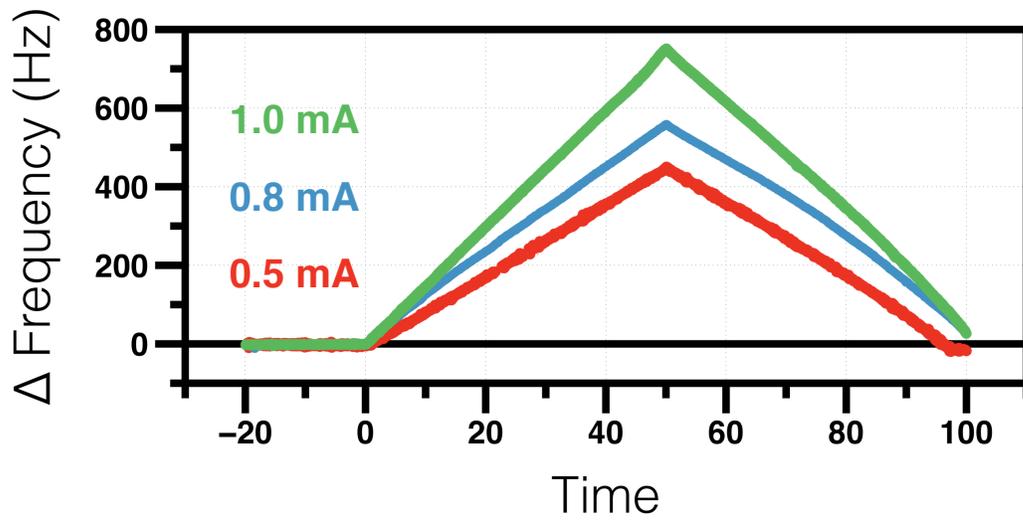
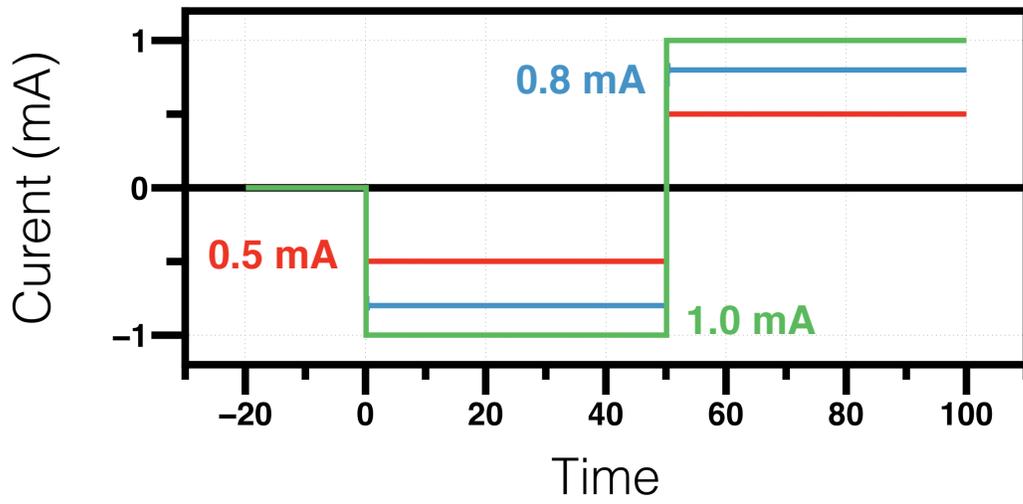
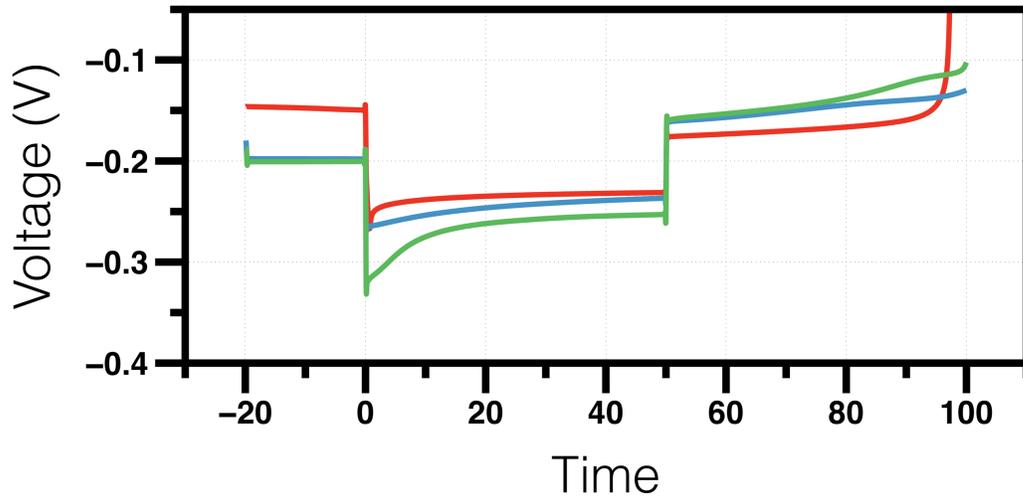
11. Start Experiment and collect data. the frequency should begin to decrease as Cu is deposited. This can be seen in the srsqcm200 program.

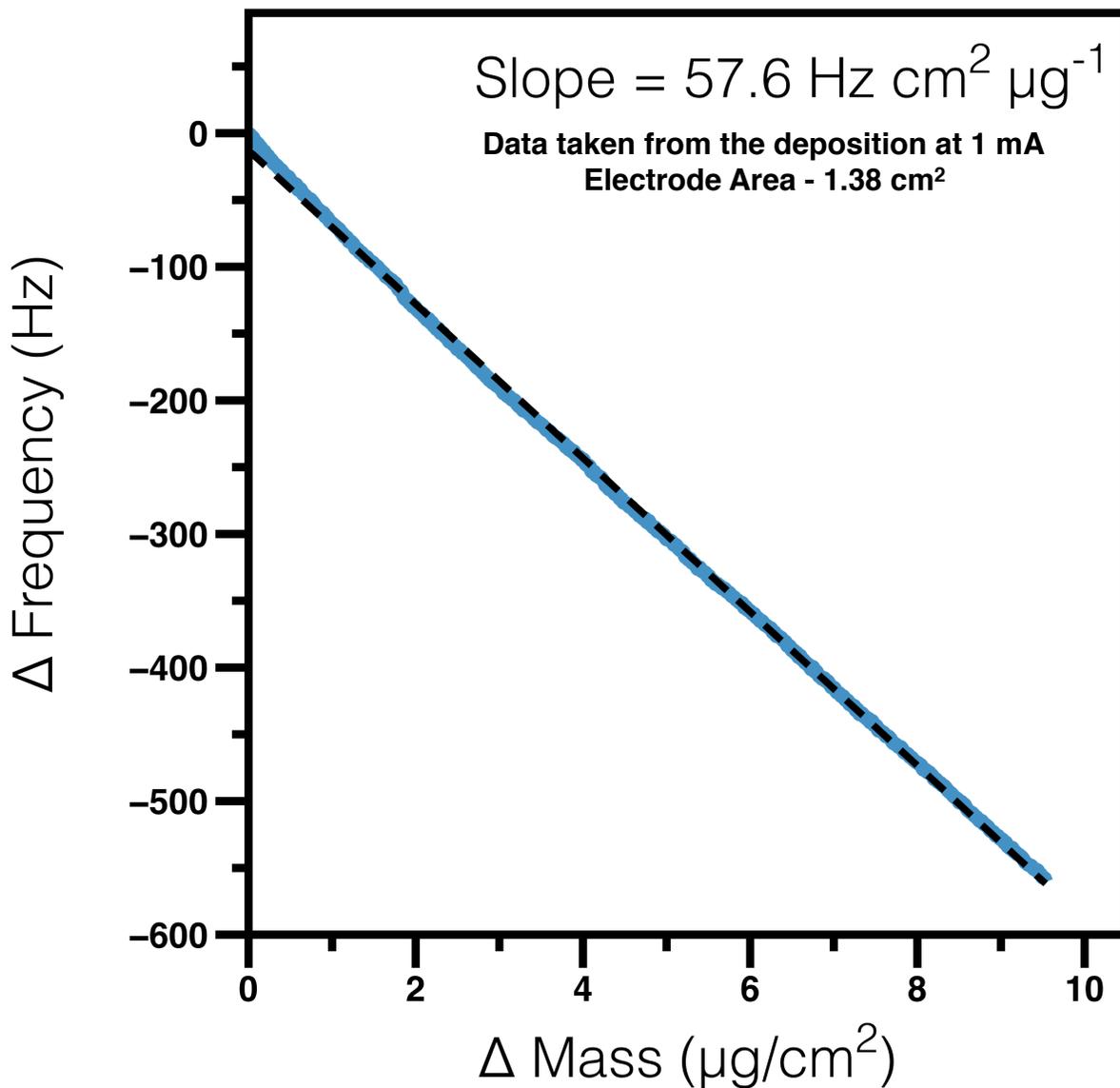
## 4.Data analysis and Work-up

1. Open the data in EChem Analyst and add the data from the auxiliary channel (Ach) to the dataset. This data is the voltage from the QCM which can be used to calculate the change in frequency at each point in time. The current data is used to calculate the theoretical mass change based on the coulombs passed. Again notice that a more positive voltage means an increase in mass, which is accompanied by a the passage of a negative current (cathodic). This negative current causes Cu deposition on the surface of the electrode.



## 4.Example Data





## References

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